1-1-2012

Armouring by precipitates and the associated reduction in hydraulic conductivity of recycled concrete aggregates used in a novel PRB for the treatment of acidic groundwater

Punyama Pathirage
University of Wollongong, pp695@uowmail.edu.au

Buddhima Indraratna
University of Wollongong, indra@uow.edu.au

Long Duc Nghiem
University of Wollongong, longn@uow.edu.au

Laura Banasiak
University of Wollongong, lbanasia@uow.edu.au

Gyanendra Regmi
University of Wollongong, gr524@uowmail.edu.au

Armouring by precipitates and the associated reduction in hydraulic conductivity of recycled concrete aggregates used in a novel PRB for the treatment of acidic groundwater

Punyama Udeshini Pathirage[1], Buddhima Indraratna[2] PhD, FTSE, FIEAust, Long Duc Nghiem[3] PhD, Laura Banasiak[4] PhD and Gyanendra Regmi[5]

[1]PhD Candidate, Centre for Geomechanics and Railway Engineering, University of Wollongong, Wollongong City, NSW 2522, Australia; PH (+61) 2 4221-2325; email: pp695@uowmail.edu.au
[2]Professor of Civil Engineering and Research director, Centre for Geomechanics and Railway Engineering; Program Leader, ARC Centre of Excellence for Geotechnical Science and Engineering; University of Wollongong, Wollongong City, NSW 2522, Australia; Tel: (+61) 2 4221-3046; Fax: +61 2 4221-3238; email: indra@uow.edu.au
[3]Associate Professor, Centre for Geomechanics and Railway Engineering, University of Wollongong, Wollongong City, NSW 2522, Australia; Tel: (+61) 2 4221-4590; Fax: (+61) 2 4221-3238; email: longn@uow.edu.au
[4]Research Fellow, Centre for Geomechanics and Railway Engineering, University of Wollongong, Wollongong City, NSW 2522, Australia; Tel: (+61) 2 4221-5993; Fax: (+61) 2 4221-3238; email: lbanasia@uow.edu.au
[5]PhD Candidate, Centre for Geomechanics and Railway Engineering, University of Wollongong, Wollongong City, NSW 2522, Australia; email: gr524@uowmail.edu.au

ABSTRACT

Acidic groundwater generated from acid sulphate soil (ASS) is a major geo-environmental problem in Australia. A permeable reactive barrier (PRB) with recycled concrete aggregates as the reactive material has received considerable attention as an innovative, cost effective technology for passive treatment of acidic groundwater in ASS terrain. Laboratory column experiments conducted at the University of Wollongong investigated the acid neutralisation behaviour of recycled concrete and its potential to remove dissolved aluminium (Al) and iron (Fe). The recycled concrete effectively treated the acidic groundwater, resulting in near-neutral effluent pH and complete removal of Al and Fe. However, armouring of the concrete by precipitated secondary Al- and Fe-bearing minerals reduced the acid neutralisation capacity of the concrete by ~50%. Hence, it is of utmost importance to analyse quantitatively the effect of armouring on the surface of the reactive material. This study assesses the reduction in hydraulic conductivity caused by secondary mineral precipitation in the treatment of acidic groundwater under two operating conditions: constant flow rate and constant head. The precipitated volumes of secondary minerals were obtained from stoichiometric calculations using measured changes in their aqueous concentrations. The Kozeny-Carman equation and Darcy's Law were adopted to measure the hydraulic conductivity at different pore volumes. While the results revealed almost similar reductions in hydraulic conductivity with respect to time under both operating conditions, the hydraulic conductivity reduction under constant flow rate was faster than in the case of constant head.

Keywords: acid sulphate soils, armouring, hydraulic conductivity, permeable reactive barrier

1 INTRODUCTION

Acidic groundwater generated from acid sulphate soils (ASS) has caused many environmental problems around coastal Australia since the 1960s (White et al. 1997). Sulphidic soils containing mainly pyrite are commonly exposed to air due to the excessive use of large-scale artificial drainage to reclaim land for development and agricultural purposes. Once this sulphidic soil is exposed to air, sulphides in the soil oxidise to sulphuric acid (H_2SO_4). The environmental problem of international importance arises with the release of highly concentrated toxic metals such as aluminium (Al) and iron (Fe) along with the acidic water (Regmi et al. 2011).

Although research has been undertaken on ASS for more than five decades in Australia by many researchers (Singer et al. 1970, White et al. 1997) comparatively limited studies have been conducted for its remediation (Regmi et al. 2009). Research for controlling pyrite oxidation in ASS had not been carried out until massive fish and oyster kills were found due to the low pH, low dissolved oxygen content and high amounts of soluble aluminium in coastal rivers in the 1980's (Indraratna et al. 2010). Several techniques such as one-way floodgates and modified two-way floodgates have been utilised successfully in coastal lowland in southeast New South Wales (NSW, Australia, for preventing pyrite

oxidation and treating the resultant acidic groundwater. However, due to the risk of flooding in these low-lying areas and the oxidation of pyrite even under submerged conditions, these methods were not appropriate in the long-term (Indraratna et al. 2005).

Amongst the ASS remediation methods researched by the ASS research team at the University of Wollongong, the approach of a permeable reactive barrier (PRB) seems to be the most appropriate and cost effective remediation tool for these low-lying coastal areas. A PRB was installed on Manildra Group's environmental farm near Broughton Creek in the Shoalhaven Floodplain, southeast NSW, Australia in October 2006. The selection of an appropriate reactive material plays a considerable role in PRB design, because it will ultimately determine the reactivity and metal removal capacity of the PRB. Recycled concrete aggregates were chosen among 25 potential alkaline materials due to its potential (i) to neutralise the groundwater acidity and (ii) to remove the dissolved heavy metals such as Al and Fe from the acidic groundwater (Golab et al. 2006). The removal of Al and Fe is achieved by precipitation out of solution as Al and Fe oxy/hydroxides. Recycled concrete is a cost effective and readily available material for the treatment of acidic groundwater. Recycled crushed concrete has proven to be a strengthening material in pavement subbase applications with recycled glass (Ali et al. 2012) and to prepare high quality concrete materials (Mostafa et al. 1996, Torben et al. 1983).

Although PRBs can be successful in groundwater remediation, they might also undergo significant reductions in permeability because of chemical armouring and physical clogging caused by the accumulation of fine particles on the surfaces and in the pores of the reactive media, respectively (Mackenzie et al. 1999, Puls et al. 1999, Phillips et al. 2000, Kamolpornwijit et al. 2003). Hence, armouring and clogging will directly affect the long-term performance of the PRB (Regmi et al. 2009, Indraratna et al. 2010). Four column experiments carried out under different conditions (Regmi et al. 2011) revealed that the acid neutralisation capacity of recycled concrete was reduced by 50% due to chemical armouring. This paper summarises the resulting hydraulic conductivity reductions caused by this armouring effect in two column experiments carried out under constant flow and constant head conditions. The Kozeny-Carman equation and Darcy's Law were adopted to measure the hydraulic conductivity at different pore volumes (i.e. PV defined here as the void volume of the column).

2 MATERIALS AND METHODS

2.1 Laboratory column experiments

The recycled concrete used in the constant flow and constant head experiments was a waste material discarded after the demolition of old concrete structures. For both the column experiments, the particle size distribution was well distributed and the particle sizes ranged from 1.18-9.5 mm. The coefficient of uniformity (C_u) was 3.1 and coefficient of curvature (C_c) was 1.63. The chemical composition of the major cations in the recycled concrete is predominantly Ca (57.3%), Fe (21.4%), Al (9.85%), Mg, (5.27%), Si (3.06%) and others (3.04%) in weight (Regmi et al. 2011). The experiments were conducted in two transparent acrylic columns (ID × L = 5 cm × 65 cm) packed with a 5 cm sand ball at the bottom followed by 50 cm of crushed recycled concrete, and topped with another 5 cm sand ball. Synthetic acidic water (Table 1) was prepared as the input solution for the columns, such that comparable to the characteristics in the average groundwater from ASS terrain in southeast of NSW, Australia presented by Regmi et al. (2009).

Table 1: Water Chemistry of the influent solution prepared for column experiment simulating the water chemistry of the acidic groundwater in ASS terrain presented in Regmi et al. (2009)

Parameter	pH	ORP [a]	Acidity [b]	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	Fe^{3+}	Cl^-	SO_4^{2-}
Unit	-	mV	mmol eq/L	mmol/L							
Values	2.67	610	6.45	19.14	1.07	2.84	3.7	1.5	1.5	23.0	12.10

[a] ORP – Oxygen Reduction Potential
[b] Acidity was measured equivalent with respect to $CaCO_3$.

For the constant flow experiment (Column 1), the influent was pumped from the bottom to the top of the column at a flow rate of 2.4 mL/min using a Masterflex peristaltic pump, as shown in Figure 1A. Based on this flow rate, the retention time for one PV (534 mL for the constant flow rate experiment) is 3.70 hrs, which is 26 times smaller than the retention time for an estimated groundwater flow rate of 30 cm/day at the PRB field site. The column setup for the constant head experiment (Column 2,

Figure 1B) was similar to that of the constant flow rate apparatus. However, the column was connected to a 20 L constant head tank designed to provide a constant pressure to the column apparatus. The pressure head drop was chosen to provide an initial flow rate of 1.66 mL/min and the pressure head drop was kept constant throughout the duration of the experiment. The flow rate, which decreased with time because of particle accumulation inside the pore spaces was measured and recorded by an electronic balance at regular time intervals. The constant head column was run until the flow of synthetic water through the column had stopped. The average total porosities of the reactive material in Column 1 and 2 were 0.52 and 0.50, respectively, giving total PVs of 534 mL and 488 mL, respectively. The effluents collected in both experiments were analysed for Al and Fe concentration using atomic absorption spectroscopy (AAS).

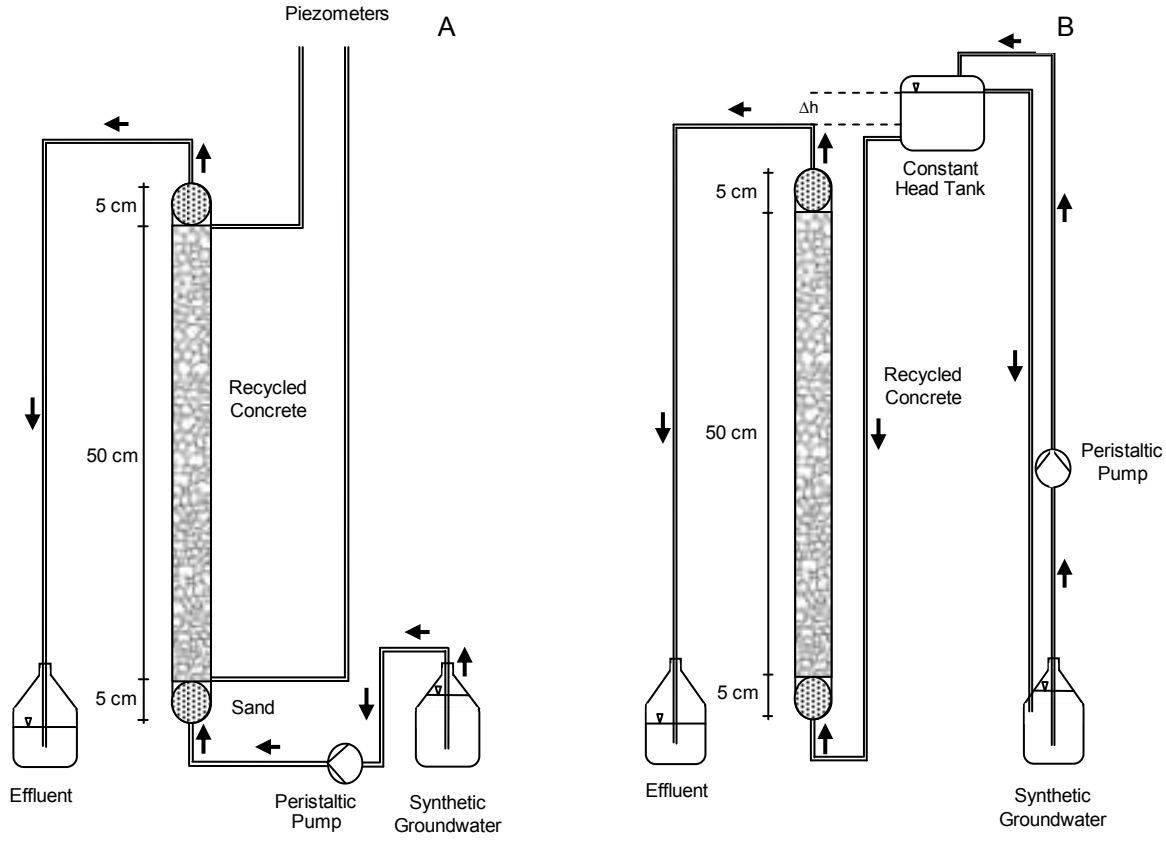

Figure 1. Experimental set up for the (A) constant flow and (B) constant head experiments

2.2 Hydraulic conductivity reduction calculation

According to mineralogical analysis performed by Regmi et al. (2009), numerous Al and Fe minerals precipitate out of solution. However, in order to simplify the stoichiometric calculations carried out to analyse quantitatively the precipitated mineral volumes only $Al(OH)_3$ and FeOOH were chosen. Darcy's Law (Equation 1) was adopted to calculate the initial hydraulic conductivity under both constant flow and constant head conditions:

$$Q = KiA \tag{1}$$

where, Q is the flow rate; K is the hydraulic conductivity; i is the hydraulic gradient; and A is the cross sectional area of the recycled concrete sample. The Kozeny Carmen equation was used to estimate the hydraulic conductivity at different PVs with the change of precipitated minerals with time:

$$K = \frac{1}{5M^2}\left(\frac{\rho_w g}{\mu}\right)\frac{n^3}{(-n^2)} \tag{2}$$

where, n is the porosity of the reactive medium, M is the specific surface of the recycled concrete particles (ratio of surface area and bulk volume), p_w is the density of water, g is the gravitational constant, and μ is the absolute viscosity of water. Mineral precipitation and dissolution may change M. However, the relationship is a complex function of the geometry of the recycled concrete particles, the shape of the minerals being precipitated, and the location of the mineral precipitates. Thus, M was assumed constant, which is a conservative approach (Li et al. 2005). Equation 2 can be used to calculate the initial porosity (n_0) and initial hydraulic conductivity (K_0) as well as the porosity (n_0-Δn_t) and hydraulic conductivity (K) at time t:

$$K = K_0 \left[\frac{n_0 - \Delta n_t}{n_0} \right]^3 / \left[\frac{1 - n_0 + \Delta n_t}{1 - n_0} \right]^2 \quad (3)$$

where, Δn_t is the reduction in porosity at time t (Li et al. 2006).

3 RESULTS AND DISCUSSION

The performance of the recycled concrete for the removal of Al and total Fe from the synthetic acidic influent is shown in Figure 3A and B. In both the constant flow and constant head experiments, the removal of Al is 100% until 200 PVs, whereby the removal significantly decreases. In the case of Fe, removal is ~95% throughout the experiments. The dissolved Al and Fe in the effluent were precipitated in the oxy/hydroxide form (Regmi et al. 2009), which were clearly visible by the considerable amount of milky white and brown-orange precipitates, respectively, in the columns. This chemical armouring and the subsequent reduction in porosity within the column reduce the reactivity of recycled concrete and, thus, the longevity.

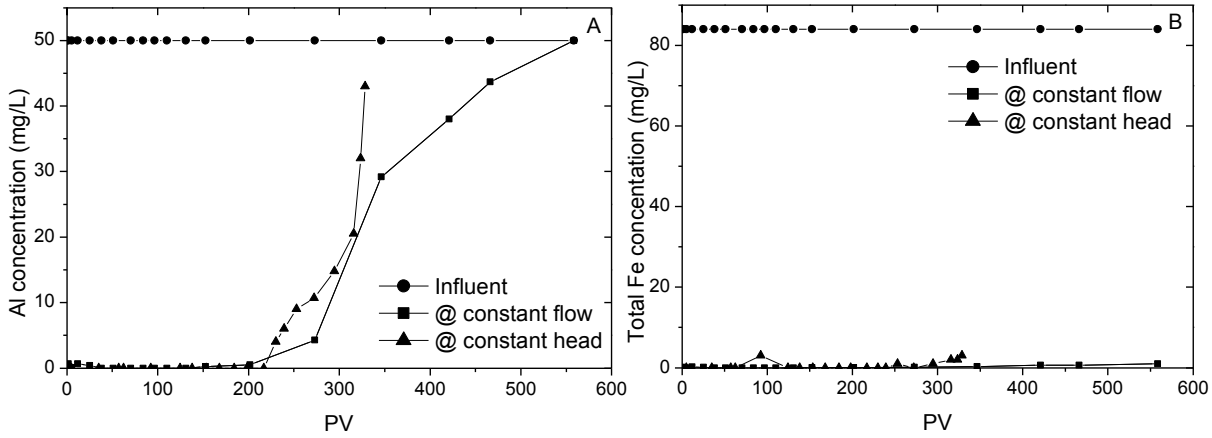

Figure 3. (A) Al and (B) Total Fe concentrations vs. number of pore volume

The hydraulic conductivity of the columns, normalised by the initial hydraulic conductivity, are plotted against the number of PVs (Figure 4). The initial hydraulic conductivity calculated from Equation 1 was 9.8 x 10^{-4} m/s at a constant flow rate of 2.4 mL/min and 2.35 x 10^{-4} m/s at a constant head drop of 3 cm for the constant flow and constant head experiments, respectively. It can be seen that the accumulation of secondary minerals reduces the hydraulic conductivity by ~20% and at the end of the constant flow experiment. In the constant head experiment, the reduction in hydraulic conductivity was ~13% when the effluent flow was zero and the experiment was terminated.

In the constant head experiment, the flow rate gradually decreased to zero (at 330 PVs) due to secondary mineral accumulation in the pore spaces (Figure 5). Since the amount of acidic water flowing through the column was decreased, the reaction with recycled concrete was also reduced with time. This resulted in a lower amount of secondary minerals being precipitated compared to the constant flow experiment. On the other hand, the constant flow experiment allowed for the constant flow of acidic water and continual reaction with recycled concrete, and increased precipitation of secondary Al and Fe minerals. This was understood to be the reason for the faster reduction in hydraulic conductivity in the constant flow experiment compared to the constant head experiment.

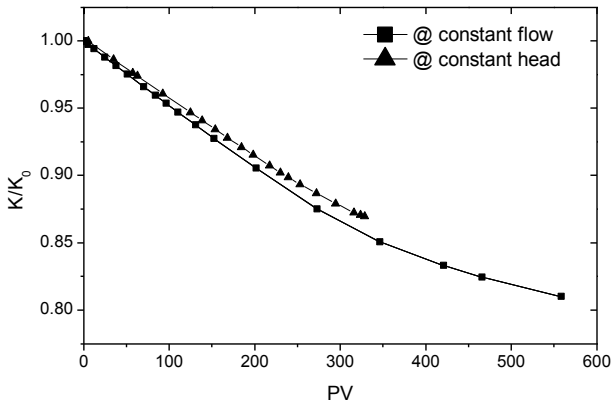

Figure 4. Normalised hydraulic conductivity vs. pore volume

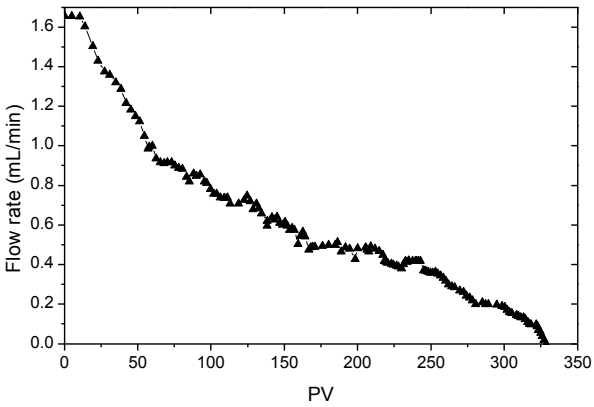

Figure 5. Flow rate vs. pore volume in constant head experiment

4 PRACTICAL APPLICATIONS

The untreated groundwater near Broughton Creek in the Shoalhaven Floodplain, where the pilot scale PRB is installed (Figure 6A and B), is acidic and has high concentrations of dissolved Al (~ 40 mg/L) and Fe (~ 250 mg/L) (Indraratna et al. 2010). Frequent monitoring of groundwater since installation of the PRB in 2006 showed that most of the Al and Fe contained in the groundwater precipitated rapidly (Figure 7A and B) when alkaline minerals from the recycled concrete started to dissolve and react. Throughout this period, the PRB was able to maintain the Al and Fe concentration below average values of 0.5 mg/L and 2 mg/L, respectively, inside the PRB indicating the excellent removal efficiency of recycled concrete for Al and Fe.

Figure 6. (A) Pilot-scale PRB with piezometers and monitoring wells in ASS terrain on Shoalhaven Floodplain, southeast NSW and (B) installation of the PRB

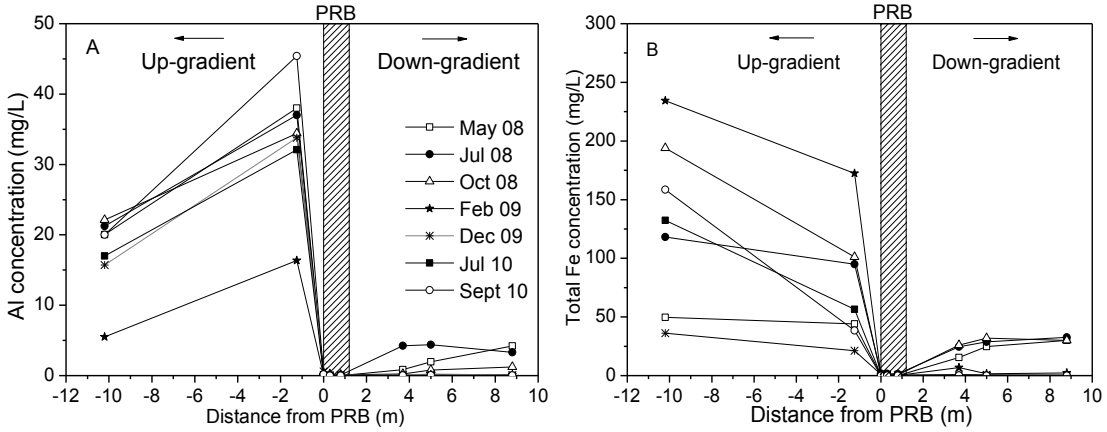

Figure 7. (A) Al and (B) Total Fe concentrations of the groundwater after installation of the PRB (Adapted from Regmi et al. (2009))

5 CONCLUSION

This study assessed differences in the reduction of hydraulic conductivity under constant flow rate and constant head for column experiments undertaken to determine the neutralisation reactions occurring between recycled concrete aggregates and synthetic acidic groundwater. Recycled concrete had the ability to remove ~95% dissolved Al and total Fe from the acidic influent; thus, confirming its suitability for remediating acidic water from ASS terrain. The resulting armouring of the surface of the recycled concrete by secondary Al and Fe oxy/hydroxide minerals was visually observed. Using measured changes in the aqueous concentration of Al and Fe, stoichiometric calculations were carried out to quantify the precipitated secondary mineral volume and subsequent reduction in porosity. The Kozeny-Carman equation was used to measure the reduction in hydraulic conductivity. A similar reduction in hydraulic conductivity with respect to PV and time was noted under both constant flow and constant head. However, the reduction rate of hydraulic conductivity under constant flow rate ($2.4x10^{-11}$ m/s^2) was 10 times faster than the reduction rate under constant head ($1.5x10^{-12}$ m/s^2).

6 ACKNOWLEDGEMENTS

The authors would like to acknowledge Glenys Lugg (Manildra Group) and Bob Rowlan (University of Wollongong) for their assistance during this study. The first and last author's PhD study was sponsored through the Endeavour Scholarship Scheme by the Australian Government.

REFERENCES

Ali, M. M. Y., and Arulrajah, A. (2012). "Potential use of recycled crushed concrete – recycled crushed glass blends in pavement subbase applications." Proceedings of GeoCongress 2012, ASCE, 3662-3671.

Golab, A. N., Peterson, M. A., and Indraratna, B. (2006). "Selection of potential reactive materials for a permeable reactive barrier for remediating acidic groundwater in acid sulphate soil terrains." Quarterly Journal of Engineering Geology and Hydrogeology, 39 (2), 209-223.

Indraratna, B., Golab, A., Glamore, W., and Blunden, B. (2005). "Acid sulphate soil remediation techniques on the Shoalhaven River Floodplain, Australia." Quarterly Journal of Engineering Geology and Hydrogeology, 38 (2), 129-142.

Indraratna, B., Regmi, G., and Nghiem, L. D. (2010). "Performance of a PRB for the remediation of acidic groundwater in acid sulphate soil terrain." Journal of Geotechnical and Geoenvironmental Engineering, ASCE 136 (7), 897-906..

Kamolpornwijit, W., Liang, L., West, O. R., Moline, G. R., and Sullivan, A. B. (2003). "Preferential flow path development and its influence on long-term PRB performance: column study." Journal of Contaminant Hydrology, 66 (3-4), 161-178.

Li, L., and Benson, C. H. (2005). "Impact of fouling on the long-term hydraulic behaviour of permeable reactive barriers." Ground Water, 43 (4), 582-596k.

Li, L., Benson, C. H., and Lawson, E. M. (2006). "Modelling porosity reductions caused by mineral fouling in continuos-wall permeable reactive barriers." Journal of Contaminant Hydrology, 83 (1-2), 89-121.

Mackenzie, P. D., Horney, D. P., and Sivavec, T. M. (1999). "Mineral precipitation and porosity losses in granular iron columns." Journal of Hazardous Materials, 68 (1-2), 1-17.

Mostafa, T. And Soroushian, P. (1996). "Strengths of recycled aggregate concrete made using field-demolished concrete as aggregate." Materials Journal, 93 (2), 178-181.

Phillips, D. H., Gu, B., Watson, D. B., Roh, Y., Liang, L., and Lee, S. Y. (2000). "Performance evaluation of a zerovalent iron reactive barrier: Mineralogical characteristics." Environmental Science & Technology, 34 (19), 4169-4176.

Puls, R. W., Blowes, D. W., and Gillham, R. W. (1999). "Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard Support Center, Elizabeth City, North Carolina." Journal of Hazardous Materials, 68 (1-2), 109-124.

Regmi, G., Indraratna, B., and Nghiem, L. D. (2009). "Effective remediation of groundwater in acid sulphate soil terrain." Australian Geomechanics Journal, 44 (4), 33-40.

Regmi, G., Indraratna, B., and Nghiem, L. D. (2009). "Long-term Performance of a Permeable Reactive Barrier in Acid Sulphate Soil Terrain." Water, Air, & Soil Pollution: Focus, 9(5-6), 409-419.

Regmi, G., Indraratna, B., Nghiem, L. D., and Golab, A. N. (2011). "Treatment of Acidic Groundwater in Acid Sulphate Soil Terrain Using Recyced Concrete: Column Experiments," Journal of Environmental Engineering, ASCE,137 (6), 433-443.

Singer, P. C., and Stumm, W. (1970). "Acidic mine drainage: The rate-determining step." Science, 167 (3921), 1121-1123.

Torben, C. H. and Narud, H. (1983). "Strength of recycled concrete made from crushed concrete coarse aggregate." Concrete International, 5 (1), 79-83.

White, I., Melville, M. D., Wilson, B. P., and Sammut, J. (1997). "Reducing acidic discharges from coastal wetlands in eastern Australia." Wetlands Ecology and Management, 5 (1), 55-72.